Introduction

In this chapter an overview of the dilute magnetic semiconductor is presented. It briefly describes the importance of non-magnetic dopant in dilute magnetic semiconductors. Moreover provides motivation and short outline of the chapters presented in this dissertation.
1.1 Introduction and background

Since research in magnetic semiconductors initiated the beginning of last century it has been noticed that in many semiconductor crystals, substitution of transition metal elements for a host element adds local magnetic moments to the system’s low-energy degrees of freedom$^{1,2}$. These doped systems are known as diluted magnetic semiconductors (DMSs). The study of DMS flourished in last two decades, when high quality samples became available for experiments and nowadays DMS are widely believed to be the ideal material for spintronics. The term “spintronics” stands for spin transition electronics, which could be the next step in the development of integrated circuits and high-frequency devices used for information processing and communications. The emerging field of spin-electronics means to incorporate the electronic spin and charge degrees of freedom into a single device$^{3-5}$.

1.2 Diluted magnetic semiconductor (DMS) materials

Two major criteria are considered when selecting the most promising materials for semiconductor spintronics. First, ferromagnetism should be retained at practical temperatures, namely at room temperature. Second, it would be a major advantage if there were already an existing technology base for the material in other applications. A breakthrough in research on magnetic semiconductors was the discovery magnetic behaviour in chromium spinels$^6$ and europium chalcogenide$^7$ films. These films were grown with built-in magnetic atoms and showed very low Curie temperature $T_C$ (50 K or lower)$^8$. Later on, interest spread to transition metal (mainly Mn) doped II-VI, IV-VI and II-V compound semiconductors. A game changer in the field was the introduction of molecular beam epitaxy (MBE) by Munekata et al.$^2$ who successfully grew the III-V material InMnAs, and observed ferromagnetism in $p$ type InMnAs. In 1996, Ohno et al.$^9$ made the first Mn doped dilute magnetic semiconductor (Ga, Mn)As. However, the magnetic transition temperature of GaMnAs is still below room temperature, $i.e$ 170K. So an important step for DMS to be used in real applications is to improve $T_C$. Many new DMS materials have been discovered in recent research, such as Mn doped CrAs$^{10}$, (Ti,Co)O$_2$$^{11}$, (Zn,Co)O$^{12}$ and Co-doped SnO$_2$$^{13}$.
1.3 Issues with transition metal doped based DMS and search for non-magnetic dopants

A particular incentive for the experimentalists were the calculations of Diet et al.\textsuperscript{14} who showed that Mn-doped ZnO would exhibit ferromagnetism above room temperature. Sato et al.\textsuperscript{15} have also reported ferromagnetic ordering of $3d$ transition metal (TM) ions in ZnO.\textsuperscript{16} There has been a wide distribution in the magnetic properties reported for transition metal doped ZnO, TiO$_2$, SnO$_2$, In$_2$O$_3$ and Cu$_2$O etc.\textsuperscript{17, 18} Experiments have now covered a broad range of parameters, including various TM dopants, compositional variations, preparation techniques and growth conditions, and post-growth processing. The observed results are often conflicting and non-reproducible between research groups. The discrepancies in the observed properties and in their interpretation likely stem from the different growth techniques and insufficient characterization. Most of the difficulties arise in determining if the material is a true DMS (TM atoms randomly substituting cation lattice sites) or if ferromagnetism originates from TM clustering or dopant-induced secondary phases. In any case, the results indicate that the underlying mechanisms of ferromagnetism in oxide diluted magnetic semiconductors (ODMS) such as ZnO and SnO$_2$ discussed in this thesis, are quite sensitive to the growth conditions and must be clearly described by careful analysis. It was noticed that ferromagnetism (FM), albeit weak, could sometimes be seen in systems with no dopants but only some native defects \textit{i.e.} ZnO,\textsuperscript{19} SnO$_2$,\textsuperscript{20} in some cases there were non-magnetic\textsuperscript{21-24} dopants that generated or enhanced the FM and in other cases non-magnetic co-dopants or defects could be observed to cooperate to develop and stabilize ferromagnetism\textsuperscript{25, 26}. These effects were found to depend on the microstructure, \textit{i.e.} grain or particle size\textsuperscript{24} and grain boundary area\textsuperscript{27}, as well as on the type and concentration of various defects, namely cation\textsuperscript{12} and anion\textsuperscript{28} vacancies or interstitials\textsuperscript{29}. Thus the search for DMS opened up the entirely new area of defect ferromagnetism and the so-called $d^0$ ferromagnetism centred on the possibility that ferromagnetic semiconductors could be developed by suitable control of dopants and engineered defects that avoid the problems of phase segregation and clustering encountered in conventional magnetically doped semiconductors.
1.4 Crystal structure of ZnO and SnO2

ZnO is a II-VI compound semiconductor whose ionicity resides at the borderline between a covalent and an ionic semiconductor\(^\text{30}\). It crystallizes in the hexagonal wurtzite-type structure shown in Figure 1.1. It has a polar hexagonal axis, the c-axis, chosen to be parallel to z. The primitive translation vectors a and b lie in the x–y plane, are of equal length, and include an angle of 120°. The point group is in the various notations 6 mm or C\(_{6v}\), the space group P6\(_3\)mc or C\(_{4v}\). One zinc ion is surrounded tetrahedrally by four oxygen ions. The primitive unit cell contains two formula units of ZnO.\(^\text{31}\) At room temperature the values of the primitive translation vectors are, \(a = b = 3.249 \, \text{Å}\) and \(c = 5.206 \, \text{Å}\) (JCPDS card no. 36-1451).

![Figure 1.1 Unit cell of the crystal structure of ZnO; yellow = Zn; blue = O. (From Wikipedia.)](image)

SnO\(_2\) (cassiterite) is known to crystallize in the rutile structure formed by a tin atom in the centre, surrounded by six oxygen atoms at the vertexes. The tin atom is bonded to four oxygen atoms with the same bond length in the basal plane and with another two apical oxygen atoms (Figure 1.2). The sublattice of Sn\(^{4+}\) ions is body centred tetragonal, \(c\) being much smaller than \(a\), \(c/a = 0.644\) and the space group P4\(_2\)/mm or D\(_{14h}\) (SG136)\(^\text{32}\) under ambient conditions. The calculated equilibrium lattice parameters for rutile SnO\(_2\) are \(a=4.738\, \text{Å}\) and \(c=3.187\, \text{Å}\) (JCPDS File No. 41-1445 Å).
In the case of SnO₂, nanoparticles have been selected as the preferred form for the system due to the ease of preparation and the availability of the preparation facilities as well as the notion that applications would ultimately very often require the incorporation of the DMS in the form of small particles.

1.5 Motivation of the thesis

The search for reproducible and verifiable ferromagnetic behaviour in the ODMS system is far from over. Following the prediction of magnetism without TM impurities, K, N, Mg, and C-doped SnO₂ moved into the focus of interest\(^{27, 34-36}\) and experimental reports clearly demonstrated room temperature FM induced by light elements in ZnO\(^{37}\). However, the exact nature of magnetism in these semiconductor oxides is still under debate.

It remains an intriguing question in itself as to how a non-magnetic dopant can develop a magnetic moment in these systems. Defects play an important role and the dopants can also combine with some of the structural defects and the parent atoms in complexes. How this influences the development of long-range ferromagnetic order is up to now not fully understood and anomalous features such as high Tₘ’s in combination with low moments are yet to be explained.

The main focus of this thesis is the development of ferromagnetism in ZnO and SnO₂ in the presence of non-magnetic dopants, namely carbon in ZnO thin films and powders, and Zn, Li in SnO₂ nanoparticles, and the role that defects play in this regard.
There still exists the specific question of whether substitutional or interstitial defects play a major role in stabilizing ferromagnetism. The issue needs further detailed study because the models predict p-type or hole dominated ferromagnetism which is most intimately connected to the presence of the cation (i.e. zinc or tin) vacancies.

Non-magnetic elements can induce magnetism but the observed magnetism is also linked to the presence of native defects. However, the formation energies of native defects, which are important for magnetism, are very high. Oxygen vacancies (V_o) have lower formation energies but neutral V_o does not induce magnetism in oxides. Hence to realize defect magnetism experimentally requires reducing the defect formation energy of the host material (ZnO and SnO_2 in our case). We chose C, Zn, Li as dopants and shall describe in this thesis how they modify the formation energies of native defects in ZnO and SnO_2.

There are few reports which systematically investigate the ferromagnetic properties of C-ZnO, Zn doped SnO_2, Li-doped SnO_2 so far. Questions that still need an answer are how C-doping of ZnO and Zn or Li-doping of SnO_2 helps to stabilize the cation vacancies and ultimately to stabilize ferromagnetism. While a non-magnetic dopant itself and the cation vacancy can both be considered hole dopants, an oxygen vacancy, the other major defect in these systems, is an electron donor and its role also requires elucidation.

Another issue we addressed was to determine how, and up to what concentration, these non-magnetic dopants can be incorporated, so as to retain the phase, avoid clustering, and lead to enhancement of ferromagnetism of the ZnO and SnO_2 hosts.

### 1.6 Thesis organization

This dissertation is organized as follows:

**Chapter 2** details the synthesis techniques used for the preparation of thin films and nanoparticles. The general principles underlying the operation of the characterization tools and the experimental details for each characterization technique are discussed.

**Chapter 3** reports on the deposition C-doped ZnO thin films by electron beam evaporation and on their structural, electronic and magnetic properties. Role of C on ferromagnetism of ZnO thin
films by stabilizing native cation magnetic defects (in our case Zn vacancy) will be discussed.

**Chapter 4** focuses on the effect on ferromagnetism of C-doped ZnO powders sintered in either reducing (95 % Ar + 5 % H) or nitrogen atmosphere. The study of the structural, electronic, magnetic and optical properties of these materials are reported and the role of carbon-related defects for the stabilization of the magnetic moment in the presence native point defects is illustrated.

**Chapter 5** reports on Sn$_{1-x}$Zn$_x$O$_2$ (x≤0.1) hierarchical architectures synthesized by a solvothermal route. Detailed results of the structural, electronic and magnetic characterization of Zn-doped SnO$_2$ hierarchical nanoparticles are explained in the light of recent computational studies that discuss the relative stability of ferromagnetic defects on various surfaces.

**Chapter 6** describes the results of Raman spectroscopy, photoluminescence and optical characterization of the Sn$_{1-x}$Zn$_x$O$_2$ (x ≤ 0.1) hierarchical architectures introduced in chapter 5.

**Chapter 7** concentrates on Sn$_{1-x}$Li$_x$O$_2$ nanoparticles synthesized by a solvothermal route and in particular on the development of ferromagnetism in SnO$_2$ due to the non-magnetic dopant. Li incorporation as substitutional or interstitial defect is investigated by X-ray photoemission spectroscopy (XPS). Different size regimes of Sn$_{0.96}$Li$_{0.04}$O (0 ≤ x ≤ 0.1) are explored to understand their effect on ferromagnetism in SnO$_2$.

The **Summary** explains the main conclusions of our studies and gives a perspective for further work.

**References**


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